



INDIAN PATENT OFFICE

IN190431

(12)INDIAN PATENT SPECIFICATION

(11) Patent No. 190431		(45) Date of Publication of Granted Patent 26/07/2003 Journal No. 30/2003	
(21)Patent Application No. 955/DEL/1995		(71)Applicant : COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH	
(24) Date of filing : 25/05/1995			
(51) Int : C07C 121/00		(72) Inventor : 1.SHIVANAND JANARDAN KULKARNI 2.REVUR RAMACHANDRA RAO 3.MACHIRAJU SUBRAHMANIAM 4.SURESH FARSI NAVIS 5.PANJA KANTA RAO 6.ALLA VENKAT RAMA RAO	
(51) Agent :			
(24) PCT Internation Application No.		(24) PCT International filing Date. NA	
(30)Priority Details.			
(33) Convention Country(s).		(31) Application No(s).	(32) Priority Date.
NA		NA	:NA
(54) Title of the invention : AN IMPROVED PROCESS FOR THE PREPARATION OF CYANOPYRIDINES			
(57) Abstract: An improved process for the preparation of cyanopyridines ; which comprises passing a feed consisting of 3-picoline or 4-picoline ammonia in a molar ratio ranging from 1:1 to 1:20 water and air/oxygen ranging from 30 cc per min. to 100 cc per min. over a vanadium-silico-alumino-phosphate (VSAPO) catalyst prepared by the process such as herein described at a temperature in the range of 300-450 °C and weight hourly space velocity of liquid feed products in the range of 0.25 to 1.0 per hour, recovering the cyanopyridines by conventional methods.			
Complete Specification <i>View as HTML</i>			

Complete Specification

This invention relates to an improved process for the preparation of cyanopyridines. This invention particularly relates to an improved process for the preparation of nitriles such as 3-cyanopyridine and 4-cyanopyridine from 3-picoline and 4-cyanopyridine from 3-picoline and 4-picoline respectively, by reacting 3- and 4- picolines with ammonia and air in the presence of a porous vanadium-silico-aluminophosphates (VSAPO) catalyst as described and claimed, in our copending application number 963/Del/95!

In the presently known process, 3- and 4-cyanopyridines can be synthesized from ammoxidation of 3- and 4-picolines over amorphous XrO_x or 2-5

VOPO_4 supported over various supports like AFeO_x , SiO_2 - AFeO_x , Cr_2O_3 , TiO_2 .

The conventional catalysts have been amorphous in nature and not shape selective catalysts. These catalysts have been employed in mostly fixed bed reactors. The following patents have discussed the preparation of nitriles of present interest, e.g. Eur. Pat. Appl. EP 37173 (1981), US Patent 4876348 (1989), US Patent 4603 207 (1986), Eur. Pat 00371 23A1 (1981), US Patent 4603 207 (1986), Eur. Pat 0037123A1 (1981), Brit. Patent 77746 (1957), Ger. (East) DDPatent 241903 (1985), US Patent 3981879 (1976), US Patent 2839535 (1958), US Patent 2510605 (1950), US Patent 3981879 (1976). In these inventions the yield of nitrile may or may not be highly selective. Particularly high-boiling products, CO , CO_2 were formed, due to the amorphous nature of the catalysts. The high-boiling products create environmental and disposal problems.

The reaction of 3-picoline or 4-picoline was carried out over V_2O_5 - Al_2O_3 mixed oxides of V , Cr , Ti , Sb , Al or Si . The yield of 3-cyanopyridine varied from 50 to 85%; while the yield of 4-cyanopyridine was 70 to 90%. The other products were the high boiling compounds, CO and CO_2 .

The object of the present invention is to develop selective and particularly provide an improved process for the preparation of nitriles employing porous active catalytic materials. The other objective of the invention is to provide a process for the preparation of nitriles wherein the formation of CO , CO_2 and high-boiling products are minimized.

The present invention provides an improved process for the preparation of cyanopyridine for respective picolines in 50-85% yields by ammoxidation in one step with very high selectivity over VSAPO catalysts at a temperature in the range of 300 to 450 °C and weight hourly space velocity in the range of 0.25 to 1.0 per hour.

Accordingly, the present invention provides an improved process for the preparation of cyanopyridines which comprises passing a feed consisting of 3-picoline or 4-picoline ammonia in a molar ratio ranging from 1:1 to 1:20 water and; air/oxygen ranging from 30 cc per min. to 100 cc per min. over a vanadium-silico-alumino-phosphate (VSAPO) catalyst prepared by the process such as herein described at a temperature in the range of 300-450 °C and weight hourly space velocity of liquid feed products in the range of 0.25 to 1.0 per hour, recovering the cyanopyridines by conventional methods.

In an embodiment of the present invention the molar ratio of picolines and ammonia used may range from 1:1 to 1:20. In another embodiment the feed ratio of air / oxygen gas may be in the range of 30 - 100 cc. per minute.

The catalysts are prepared in general in the following way. with or without NaCl , V_2O_5 and tetrapropylammonium bromide (TPA) or tetrabutylammonium bromide (TEA) used as a template, are mixed in distilled water in the pH range of 7.0 to 12.0. The slurry is mixed for atleast 2 hrs at room temperature with constant stirring and the pH is adjusted by aqueous ammonia. The slurry was put into an autoclave for auto-claving under autogeneous pressure in the temperature range of 150 to 220 °C for 24 hrs to 80 hrs till complete crystallization was achieved. The mixture was filtered and washed with distilled water. The solid catalyst was dried in oven- at 120 °C over night. The organic template was removed by the activation of the catalyst at 400-550 °C for 5-15

hrs. Then the calcined material was modified by promoters like Sb2O3 or oxides of the elements active as promoters in the respective reactions. Basically in aluminophosphate molecular sieves the Al:P atomic ratio is 1:1. We have substituted P partially by Si or V as discussed and claimed in

the copending patent number : 1459/DEL/1995 . Al also may be substituted partially by Si with V ; the corresponding variation in the atomic ratio.

The above said reactions were carried out in a tubular,down-flow pyrex reactor with 20 mm internal diameter. The reaction mixture was fed from top using syringe pump(Sage Instruments,USA). The product was cooled by using ice-cooled water and collected at the bottom. The required number of ice-cooled traps were used to collect the total amount of products. The products were analysed by using SE-30 (5%) and OV-17 columns.The analysis was confirmed by mass spectra and GC-mass.

The ammoxidation of 4-picoline with ammonia was carried out in presence of air (O2) at 420° C with 0.5 hr⁻¹ W.H.S.V. and 4 gm of catalyst like VSAPO(TPA), VSAPO (TEA),VSAPO-37 (18-30 mesh). 4-Picoline was diluted with water in 1:3 volume ratio. The feed rate of ammonia was 30-35 cc per min and the rate of air was 60 cc per min. The following reaction parameters were varied, reaction temperature, 4-picoline : NH3, 4-picoline:H2O, W.H.S.V., etc.

The ammoxidation of 3-picoline with ammonia was carried out in presence of air (O2) at 420° C with 0.5 hr⁻¹ W.H.S.V. and 4gm of catalyst. 3-Picoline was diluted with water using 1:3 by volume ratio. The feed rate of ammonia gas was 35 cc per min and rate of air was 60 cc per min. With the increase of ammonia in the feed there was increase in the yield of 3-cyanopyridine to about 60.8 wt%. The various reaction parameters like reaction temperature, weight hourly space velocity, picoline to ammonia and water ratio in the feed were varied.

The following examples are given to illustrate the process of the present invention, however these should not be construed to limit the scope of invention.

EXAMPLE - 1

0.477 gm per hr 4-Picoline, 1.50 gm of water per hour, 0.228 gm (30 cc per min) of ammonia and 60.0 cc per min air over VSAPO(TPA) at 420° C and 0.5 hr⁻¹ weight hourly space velocity of liquid feed. The 4-Picoline to ammonia mole ratio was 1:5. The yield of 4-cyanopyridine was 79.3% based on 4-picoline at 100% conversion of 4-picoline. No deactivation was observed for more than 6 hrs time on stream. The template TPA (tetra propyl ammonium bromide) was removed before the reaction. The activity can be regenerated.

EXAMPLE - 2

In the reaction of 0.477 gm per hr of 3-picoline, 0.228 gm (30 cc per min) ammonia, 1.5 gm of water per hr and 60 cc per min air over 4 gm VSAPO(TPA-A) at 420° C, 0.5 hr⁻¹ W.H.S.V. of liquid feed ; the yield of 3- cyanopyridine was 37.2% based on 3-picoline at 59.2% conversion of 3-picoline.

EXAMPLE-3

In the reaction of 0.167 gm per hr of 4-picoline, 0.228 gm (30 cc per min) ammonia, 0.83 gm of water per hr and 60 cc per min air over 4 gm VSAPO(TPA-A) at 420° C, 0.5 hr⁻¹ W.H.S.V. of liquid feed ; the yield of 4-cyanopyridine was 96.5% based on 4-picoline at 98.6% conversion of 4-picoline.

EXAMPLE - 4

In the reaction of 0.477 gm per hr of 3-picoline, 0.228 gm (30 cc per min) ammonia, 1.5 gm of water per hr and 60 cc per min air over 4 gm Sb2O3-VSAPO(TPA-A) at 420° C, 0.5 hr⁻¹ W.H.S.V. of liquid feed; the yield of 3-cyanopyridine was: 35.2% based on 3-picoline at 43.7% conversion of 3-picoline.

EXAMPLE-5

In the reaction of 0.67 gm per hr of 4-picoline, 0.228 gm (30 cc per min) ammonia, 3.33 gm of water per hr and 60 cc per min

air over 4 gm VSAPO (TPA-A) at 420° C, 0.5 hr¹ W.H.S.V. of liquid feed: the yield of 4-cyanopyridine was 82.8% based on 4-picoline at 97.0% conversion of 4-picoline.

We claim:

1. An improved process for the preparation of cyanopyridines which comprises passing a feed consisting of 3-picoline or 4-picoline ammonia in a molar ratio ranging from 1:1 to 1:20 water and air/oxygen ranging from 30 cc per min. to 100 cc per min. over a vanadium-silico-alumino-phosphate (VSAPO) catalyst prepared by the process such as herein described at a temperature in the range of 300-450°C and weight hourly space velocity of liquid feed products in the range of 0.25 to 1.0 per hour, recovering the cyanopyridines by conventional methods.
2. An improved process as claimed in claim 1 wherein the molar ratio of picolines and ammonia used is 1:5 preferably.
3. An improved process as claimed in claims 1-2 wherein the feed ratio of air or oxygen gas is 60 cc per min. preferably.
4. An improved process for the preparation of cyanopyridines substantially as herein described with reference to the examples.